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PATENT SPECIFICATION

667,101



Date of filing Complete Specification: Feb. 1, 1950.

Application Date: Feb. 23, 1949. No. 4912/49.

Complete Specification Published: Feb. 27, 1952.

ERRATA

SPECIFICATION No. 667,101

Page 2, line 79, for " $K_4[Fe(ON)_6]$ "
read " $K_4[Fe(CN)_6]$ "

Page 2, line 83, for " $(NO)_2$ " read
" $(NO)_2$ "

Page 2, line 114, for "thereof." read
"thereof, depending on the conditions."

THE PATENT OFFICE.
11th October, 1952.

importance in industrial and export
usages, more particularly low bulk
density, ready solubility and free-flowing
characteristics.

The production of salt having these
properties has until now always involved
evaporation in conditions such that there
is an almost undisturbed air-brine inter-
face on which plate-like or hopper-shaped
crystals grow. Attempts to use multiple
effect evaporation have always yielded
cubic crystals which have a bulk density
of about 1. Many laboratory experi-
ments have been carried out to investi-
gate the effect of other substances on the
crystallisation of salt from brine, and
some have yielded hollow-faced cubes and
octahedral crystals, but not a specially
light form. Moreover, most of those
results have been obtained by crystallising
a drop of brine on a microscope slide, and
none of them have been confirmed with
conditions altered to be suitable for
evaporation on an industrial scale.

We have made a new form of salt which
has several spiky branches on each
crystal, and crystals of this shape occupy
a relatively large volume per unit weight.
It is essential to have spikes lying in more
than one plane if the crystals are to pack
voluminously, but apart from this the
size and shape of the spike are relatively

understood to have grown with at least
three main spiky or needle-shaped arms
lying in more than one plane and usually
with subsidiary arms growing from the
main arms, and to have a bulk density not
exceeding 0.7 gm. per cc.

In a preferred form the 3-dimensional
dendritic crystals are of at least 0.1 mm.
in size, generally of from 0.3 mm. to
1.0 mm. in size. In this preferred form
the crystals have a bulk density between
0.5 and 0.6 gm. per cc. The most desir-
able form of crystal also has the sub-
sidiary arms or spikes extending in more
than one plane so that even if a crystal is
accidentally broken the portions still
retain the 3-dimensional dendritic form
and the desired properties. The 3-dimen-
sional dendritic crystals are essentially
long irregular branching spiky growths
connected at the bases and generally
thicker at the base than at the tip. When
six or eight branches are roughly of
equal lengths, the highly magnified
crystals look like part of a star.

The form of salt provided by this inven-
tion does not cake in the manner in which
cubic crystals of salt cake when standing
in air. It readily dissolves in water by
percolation, it occupies a large volume
per unit weight, and in humid climates
it holds comparatively large proportions

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PATENT SPECIFICATION

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Date of filing Complete Specification: Feb. 1, 1950.

Application Date: Feb. 23, 1949. No. 4912/49.

Complete Specification Published: Feb. 27, 1952.

Index at acceptance:—Classes 1(iii), D10, G50—D10; and 32, A2e.

COMPLETE SPECIFICATION

Salt Crystals

We, WINSTON EWART MAY, of 31, Agecroft Road, Rudheath, Cheshire, and THOMAS REGINALD SCOTT, of "Long Orchard," Acton Bridge, Cheshire, both British Subjects, and IMPERIAL CHEMICAL INDUSTRIES LIMITED, of Imperial Chemical House, Millbank, London, S.W.1, a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a new and improved form of salt (sodium chloride) having certain advantages which are of importance in industrial and export usages, more particularly low bulk density, ready solubility and free-flowing characteristics.

The production of salt having these properties has until now always involved evaporation in conditions such that there is an almost undisturbed air-brine interface on which plate-like or hopper-shaped crystals grow. Attempts to use multiple effect evaporation have always yielded cubic crystals which have a bulk density of about 1. Many laboratory experiments have been carried out to investigate the effect of other substances on the crystallisation of salt from brine, and some have yielded hollow-faced cubes and octahedral crystals, but not a specially light form. Moreover, most of those results have been obtained by crystallising a drop of brine on a microscope slide, and none of them have been confirmed with conditions altered to be suitable for evaporation on an industrial scale.

We have made a new form of salt which has several spiky branches on each crystal, and crystals of this shape occupy a relatively large volume per unit weight. It is essential to have spikes lying in more than one plane if the crystals are to pack voluminously, but apart from this the size and shape of the spike are relatively

unimportant. This form of salt is relatively easily distinguished from the known forms in that it has a bulk density not exceeding 0.7 grams per cc. and on microscopic examination (at a magnification of, say 50) it is obviously spiky and unlike the low density plate-like crystals already known.

According to the present invention, therefore, the new and improved form of salt comprises 3-dimensional dendrites having a bulk density not exceeding 0.7 gm. per cc., that is to say dendritic crystals of which the characteristic dendritic arms or spikes lie in three dimensions. Such crystals will thus be understood to have grown with at least three main spiky or needle-shaped arms lying in more than one plane and usually with subsidiary arms growing from the main arms, and to have a bulk density not exceeding 0.7 gm. per cc.

In a preferred form the 3-dimensional dendritic crystals are of at least 0.1 mm. in size, generally of from 0.3 mm. to 1.0 mm. in size. In this preferred form the crystals have a bulk density between 0.5 and 0.6 gm. per cc. The most desirable form of crystal also has the subsidiary arms or spikes extending in more than one plane so that even if a crystal is accidentally broken the portions still retain the 3-dimensional dendritic form and the desired properties. The 3-dimensional dendritic crystals are essentially long irregular branching spiky growths connected at the bases and generally thicker at the base than at the tip. When six or eight branches are roughly of equal lengths, the highly magnified crystals look like part of a star.

The form of salt provided by this invention does not cake in the manner in which cubic crystals of salt cake when standing in air. It readily dissolves in water by percolation, it occupies a large volume per unit weight, and in humid climates it holds comparatively large proportions

Price

of brine without dripping. Properties of this nature have hitherto been associated with expensive open pan grades of salt, and the manufacture of the latter grades of salt is a specialised art which has been practised for centuries using open pans heated by fires beneath the pans with the object of producing crystals having an open structure. In the open pan process, the crystals are grown on the surface of the liquor and disturbance of the latter surface is avoided by evaporating the brine slowly. Thus the crystals cannot grow much in the direction perpendicular to the brine surface. Depending on the conditions in which the pan process is conducted and on additives which are dissolved in the brine, crystals varying from thin light flakes to quite thick hollow hopper-shapes are obtained. Additives used have included soap, starch, alum, glue and butter. The production of open pan salt involves the use of much fuel and labour even when modern plant with steam heating and mechanical handling is used. By comparison, the preparation of salt by multiple effect vacuum evaporation is much more efficient in fuel and labour, but it has hitherto only been capable of making compact cubic or octagonal crystals.

According to a further feature of the invention, we provide a process for the manufacture of salt of low bulk density which comprises evaporating brine containing a modifying agent as hereinafter defined, substantially in absence of air and in such a manner that crystallisation mostly takes place in the body of the brine, and with insufficient agitation to disintegrate the crystals so obtained.

By a modifying agent we mean a substance which inhibits crystallisation in the centres of the faces of the crystal, thus causing crystallisation of salt as hollow-faced cubes or hollow-faced octahedra. In extreme cases where the concentration of modifying agent is high or the agent is unusually effective, or the rate of crystallisation is high, the crystallisation is not only inhibited at the face-centres but also on the edges, thereby so accentuating the corners as to produce dendrites, which have spikes in three dimensions. They may have up to eight main spikes if unbroken, and these eight main spikes may also have subsidiary branches on each spike, and so on. The modifying agents we use belong to one of three classes of substances. The first class is the known group of substances which have the formula $A[MX_n]$ in which the complex ion MX_n has the X groups disposed around M in the same

manner as at the corners of an octahedron. These complex ions are of approximately the size which will fit on to the possible face of a growing NaCl crystal or into the NaCl lattice, thus displacing a unit which is a Na atom surrounded by six Cl atoms, or *vice versa*. This group of substances is readily adsorbed by the growing salt crystal. The preferred substances in this group are the iron compounds, particularly $K_3[Fe(C_2O_4)_3]$ in which each oxalate group provides two of the X groups, $FeK[Fe(CN)_6]$, $Na_3[Fe(NO)(CN)_5]$, $K_3[Fe(ON)_3]$ and $K_3[Fe(CN)_6]$. Other compounds which can be used include $[Co(NO_2)(NH_3)_5](NO_3)_2$, $[Co(NH_3)_4(H_2O)Cl]Cl$, and $K[Co(NH_3)_2(NO)_2]$. The second class of substances used as modifying agents are water-soluble salts of mono- or polycarboxylic acids having not more than 20 carbon atoms. Examples of this class are sodium palmitate, sodium laurate, sodium stearate, sodium gluconate, sodium formate, ammonium salicylate, sodium phthalate, ammonium maleate, potassium malate, sodium fumarate, sodium chloracetate and sodium aminoacetate. The third class of substances are very soluble in water capable of giving solutions containing 35–80% of modifying agent in which salt is generally only 1–2% soluble, and make a very viscous solution. This includes glycerol, ammonium nitrate, caustic soda, calcium chloride, ethylene glycol, mannitol, glucose, fructose, and sucrose.

The amount of modifying agent used depends on the magnitude of the effect required as well as the efficacy of the agent. In the case of ferro- and ferricyanides, between 0.00005% and 0.0005% by weight of the $A[MX_n]$ compound in the initial brine or in the feed brine of a continuous process, is sufficient to produce hollow-faced cubes or 3-dimensional dendrites at temperatures above 100° C., but we generally prefer to start with a brine containing up to 0.005% thereof. For other substances of this type, 0.02% by weight in the initial brine is generally preferred. Larger amounts of the carboxylates are needed, and some of them are not sufficiently soluble in brine to produce 3-dimensional dendrites, though they do produce hollow-faced cubes. In general, between 0.05% and 0.02% by weight of the monocarboxylic acid salts in the brine is sufficient, or between 0.5% and 2% by weight of dibasic acid salts in the brine. Between 20% and 60% by weight of the third class of substances is required in the brine in order to produce the desired effect. The proportion required is readily ascertained by trial in

each case.

The evaporation is preferably carried out by boiling at temperatures of 35°—130° C., under suitable absolute pressures. The preferred method of evaporation, particularly with the first two classes of modifying agent, is by multiple effect in order to secure the full benefits of low fuel consumption, but single effect evaporation may also be used with the generation of useful steam. In order to give the crystals an opportunity to grow to a commercially attractive size such as 0.3 mm. or larger, the evaporator, if it is of the usual multiple effect type, should be arranged so that the brine in the evaporation zone contains from 2% to 10% by weight of salt in suspension. The agitation is limited to ensure production of the desired crystal form and to avoid breaking up the crystals. If there is too much agitation, such as is produced by boiling in industrial vacuum evaporators with a rate of steam evolution as high as 4000 cubic metres of steam per square metre cross section of the evaporator body per hour, the product does not look much like 3-dimensional dendrites and has a bulk density of about 0.75 gm. per cc. Reduction of this agitation, however, soon changes the product so that it has a fluffy dendritic appearance and its bulk density falls below 0.70 gm. per cc. The reason for this may well be that disintegration of the dendrites occurs when the agitation is brisk. There is no definable unit of agitation, and in any case the permissible amount varies with the shape and type of apparatus. All that can be stated is that if the crystals obtained are insufficiently dendritic in appearance and of too high a bulk density, a decrease in agitation will produce a substantial improvement. Other types of evaporators can be used including for example forced circulation evaporators, evaporators having separate chambers for heating, evaporating and crystallising with circulation of liquor therethrough, and also pots in which the brine is boiled briskly by heating from below and the steam is withdrawn.

The invention is illustrated but not restricted by the following examples.

EXAMPLE 1.

Brine was purified of its calcium and magnesium content, and 10 parts of $K_4[Fe(ON)_6]$ were added to a million parts of brine by weight. The pH value of the brine was 10. The evaporator used consisted of a calandria for heating the brine, flash vessel, crystallising chamber, and pump to circulate the brine through this system. Vacuum was

applied so that boiling occurred in the flash vessel at a temperature of 90° C. The brine level was maintained by adding feed brine of the same composition as the initial brine. The circulation was arranged so that the crystals in the crystallising chamber remained there without being carried out by the up-flow of brine through them. The heating in the calandria was arranged so that the temperature rise of the brine was 4° C. The initial crystals added to the crystallising chamber were small cubes, but growth developed preponderantly at the corners. The accretions at the corners of the original cubes then developed further growths of a branched appearance. The crystals were kept in the suspension chamber for up to 2—3 hours. After this time they were between 0.3 and 1 mm. in length. The bulk density of the dried crystals was 0.45 gm. per cc.

EXAMPLE 2.

Brine was purified of its calcium and magnesium content, and 100 parts of potassium palmitate were added to a million parts of brine by weight. The pH value of the brine was 10. The evaporator used consisted of a closed vessel containing the brine and fitted with a steam-heated calandria, and having a steam outlet at the top and a salt outlet at the bottom. Vacuum was applied to the vessel so that the brine boiled at 80° C., and more brine was fed in.

The ebullition caused agitation of the brine in the evaporator, and the salt crystals formed remained suspended in the brine until they grew large enough to fall into the salt outlet at the bottom of the evaporator. These crystals grew preferentially along the edges and produced a low density hollow-faced cube. The crystals fell into the outlet when they approached 0.5 mm. dimension. The dried product had a bulk density of 0.7 gm. per cc.

EXAMPLE 3.

Brine was mixed with calcium chloride so that the boiling point of the solution at atmospheric pressure was 130° C. The evaporator used was a corrosion-resistant vessel directly heated by a fire. It had one steam outlet and one brine inlet and was fitted with a stirrer. Brine was added intermittently to the boiling suspension and salt was extracted after each brine addition. In the intervals between the brine additions, the evaporation gradually brought back the boiling point from about 125° C. to 130° C. The salt crystals obtained after steady conditions had been established were in the form of dendrites of a coordinate axis type and

had the appearance in some instances where the branches were short of six-pointed 3-dimensional stars. The bulk density of these salt crystals was 0.6 gm. per cc.

What we claim is:—

1. Salt in the form of 3-dimensional dendrites and having a bulk density not exceeding 0.7 gm. per cc.
2. Process for the manufacture of salt of low bulk density which comprises evaporating brine containing a modifying agent as hereinbefore defined, substantially in absence of air and in such a manner that crystallisation mostly takes place in the body of the brine, and with insufficient agitation to disintegrate the crystals so obtained.
3. Process as claimed in Claim 2 in which the modifying agent is (1) a soluble salt of a mono- or polycarboxylic

acid containing not more than 20 carbon atoms, or (2) a compound having the formula $A[MX_n]$ as hereinbefore defined, or (3) a highly water-soluble substance which is capable of producing a very viscous solution in which salt is only slightly soluble.

4. Process as claimed in claim 3 in which the brine contains a ferro- or ferricyanide.

5. Process as claimed in claim 4 in which the concentration of ferro- or ferricyanide in the initial brine is at least 0.00005% by weight.

6. Process for the manufacture of salt of low bulk density substantially as hereinbefore described with reference to each of the foregoing examples.

J. W. RIDSDALE,

Solicitor for the Applicants.

PROVISIONAL SPECIFICATION

Salt Crystals

We, WINSTON EWART MAY, of 31, Agecroft Road, Rudheath, Cheshire, and THOMAS REGINALD SCOTT, of "Long Orchard," Acton Bridge, Cheshire, both British Subjects, and IMPERIAL CHEMICAL INDUSTRIES LIMITED, of Imperial Chemical House, Millbank, London, S.W.1, a British Company, do hereby declare the nature of this invention to be as follows:—

This invention relates to a new and improved form of salt (sodium chloride) having certain advantages, e.g. low packing density, ready solubility and free-flowing characteristics, which are of importance in industrial and export usages of the salt.

According to the present invention the new and improved form of salt comprises dendritic crystals of which the characteristic dendritic arms or spikes diverge outwardly in three dimensions. Such crystals will thus be understood to have grown with at least three main spiky or needle-shaped arms lying in more than one plane and usually with subsidiary spiky arms growing from the main arms, and to have a pouring density not exceeding 0.7 gm. per cc.

In a preferred form the three-dimensional dendritic crystals are of at least 0.1 mm. in size, generally of from 0.3 mm. to 1.0 mm. in size. In this preferred form the crystals have a pouring density between 0.5 and 0.6 gm. per cc. The most desirable form of crystal also has the subsidiary arms or spikes extending in more than one plane so that acci-

dental breakage of a crystal produces separate portions which retain a three-dimensional dendritic form and the appropriate desirable properties. The three-dimensional dendritic crystals are essentially long irregular branching spiky growths connected at the bases and generally thicker at the base than at the tip. They look like part of a star.

The form of salt provided by the invention does not cake, it readily dissolves in water by percolation, it occupies a large volume per unit weight, and in humid climates it holds comparatively large proportions of brine without dripping. Properties of this nature have hitherto been associated with expensive open pan grades of salt, and the manufacture of the latter grades of salt is a specialised art which has been practised for centuries using open pans heated by fires beneath the pans with the object of producing crystals having an open structure. The crystals are grown on the surface of the liquor and disturbance of the latter surface is avoided by evaporating the brine slowly. The growth of the crystals is restricted in a direction perpendicular to the brine surface. Depending on the conditions under which the pan process is conducted and on modifying agents which are added to the brine, flakes or hollow hopper-shaped crystals of appropriate packing density are obtained. Modifying agents used have included soap, starch, alum and butter. The production of open pan salt involves the use of much fuel and labour, but the

more efficient preparation of salt crystals by multiple effect vacuum evaporation has hitherto yielded only compact cubic or octagonal crystals.

- 6 An example of a method of making salt crystals in accordance with the present invention does not involve the growth of such crystals on an air-brine interface, and comprises the evaporation of brine having a pH value of at least 7 and containing a modifying agent which inhibits growth at the centres of the cube faces. The preferred modifying agent is a soluble ferrocyanide or ferricyanide, 15 1—20 parts thereof per million parts by weight of brine being suitable, and 5—15 parts per million being preferred. Other modifying agents include complex inorganic salts, glycerine, and long chain organic salts with one hydrophilic terminal group. The preferred method of evaporation is by multiple effect in order to secure the full benefits of low fuel consumption, but single effect 25 evaporation may also be used with the generation of useful steam.
- Previously known modifying agents have not been used for evaporation except in contact with the atmosphere, which is 30 not possible in multiple effect working. This is because they do not, by themselves, have the desired effect of producing salt crystals having an open structure, when the evaporation is done out of 35 contact with the atmosphere. We have found that in our process dendritic crystals can be produced in the bulk of the liquid where crystallisation can take place in three dimensions.
- 40 The evaporation is preferably carried out by boiling at temperatures of 35°—130° C., under suitable absolute pressures, and with means for keeping the salt crystals in the evaporator so that the

brine in that zone contains about 2—5% 45 by weight of suspended salt. The agitation is limited to ensure production of the desired crystal form and to avoid breaking up the crystals.

In an example of one method of carry- 50 ing out this process, brine was purified of its calcium and magnesium content, and was modified by adding 10 parts of potassium ferrocyanide to a million parts of brine by weight. The pH value of 55 the brine was 10. The evaporator used consisted of a calandria for heating the brine, flash vessel, crystallising chamber, and pump to circulate the brine through this system. Vacuum was applied so 60 that boiling occurred in the flash vessel at a temperature of 90° C. The circulation was arranged so that the crystals in the crystallising chamber remained there without being carried out by the up-flow 65 of brine through them. The heating in the calandria was arranged so that the temperature rise of the brine was 4° C. The initial crystals added to the crystallising chamber were small cubes, but 70 gradually these cubes developed along their edges so as to produce poly-pyramidal growths or dendrites. The crystals were kept in the suspension chamber for up to 2—3 hours. After 75 this time they were between 0.3 and 1 mm. in length. The pouring density of the dried crystals was 0.45 grams per cc.

Other types of evaporator can be used, but we prefer one in which the crystals 80 are only subjected to gentle agitation, yet remain in the suspension long enough to grow to a size of about 0.3 mm. or larger.

Dated the 22nd day of February, 1949.

J. W. RIDSDALE,
Solicitor for the Applicants.